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13. ABSTRACT (Maximum 200 words)

A collaborative theoretical and experimental investigation of the non-bonding interactions of the boron atom with the hydrogen molecule and other species has been carried out. Additionally, bimolecular collisions of electronically excited boron atoms and non-bonding interactions of other boron-containing species, namely BH and the isovalent AlH radical, were investigated. The main advances from the experimental component of this program has been in the spectroscopy of weakly bound complexes of atomic boron, while those from the concurrent theoretical work has involved the elucidation of potential energy surfaces of weakly bound complexes of open-shell species.

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THE INTERACTION OF GROUP IIIA ATOMS
WITH SMALL MOLECULES

FINAL REPORT

Paul J. Dagdigian and Millard H. Alexander

The Johns Hopkins University
and The University of Maryland

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TABLE OF CONTENTS

I. SUMMARY OF WORK AND DESCRIPTION OF WORK ACCOMPLISHED

A primary goal of this work has been the theoretical and experimental investigation of the non-bonding interactions of the boron atom, in its ground and first allowed electronic state, with the hydrogen molecule and other species, with extension to other boron containing species (*e.g.* the ArBH van der Waals complex) and bimolecular collisions involving electronically excited boron atoms. The new advances arising from the experimental component of this joint research program have been in the spectroscopy of weakly bound complexes involving atomic boron and in the dynamics of bimolecular collisions of reactive atoms. Concurrently, the new advances from the theoretical component of this joint research program have involved the elucidation of potential energy surfaces of weakly-bound complexes of open-shell species and the development of new methods for the study of the dynamics of van der Waals molecules and of molecular photofragmentation. The following sections summarize our progress of these goals and presents details of our research accomplishments.

A. Experimental and Theoretical Study of the B–Ar Interaction

1. *Observation and Analysis of the B – X Spectrum of BAr.* Despite the now extensive information available on van der Waals interactions of heavier group 13 atoms (Al[1-4], In[5]) with rare gas atoms, there was no information available on such interactions involving the boron atom prior to our investigations of the BAr complex.[6-8] We have succeeded in generating and detecting BAr through 193 nm photolysis of diborane seeded in He/Ar in a pulsed supersonic beam.[6] We found that much colder beam temperatures (6 K, as measured by the atom spin-orbit temperature) were required for the generation of BAr, as compared to AlAr.

We have observed a progression of BAr (v′,0) bands in the $B^2\Sigma^+ - X^2\Pi_{1/2}$ system, which correlates asymptotically with the boron $3s\ ^2S \leftarrow 2p\ ^2P$ atomic transition. The presence of two isotopes of boron (^{10}B and ^{11}B) facilitated the assignment of the excited state vibrational quantum numbers v′, and hence the estimation of the excited state dissociation energy. An interesting feature of the spectrum is that the last two bands of the

1

progression are not rotationally resolved; indeed, the very last band is so broadened that the ^{10,11}BAr isotope splitting is not resolved. This broadening is most likely due to predissociation of these vibrational levels. This, in turn, implies that the excited $B\ ^2\Sigma^+$ state possesses a *barrier* in its potential energy curve at large internuclear separations. From the spectroscopic constants derived from the resolved bands, it was possible to compute an RKR potential energy curve for the lower portion of the $B^2\Sigma^+$ state.

2. *Calculation of the X, A, and B State Potential Energy Curves.* In conjunction with these experiments and to characterize further the B–Ar interaction, we have carried out *ab initio* calculations with a large (*spdfg*) gaussian atomic orbital basis set of the three BAr electronic states $[X^2\Pi, A^2\Sigma^+,$ and $B^2\Sigma^+]$ which correlate with the B($2p\ ^2P$, $3s\ ^2S$) asymptotes. Complete active space self-consistent field (CASSCF)[9] calculations were carried out and were followed by multi-reference, internally contracted, configuration-interaction (MR-CI) calculations.[10, 11] In addition, the effect of higher order excitations was estimated using either the multi-reference version of the Davidson correction[12] or the Averaged Coupled-Pair Functional method of Gadnitz and Alrichs.[13] From these calculations, estimates of both the ground and excited state dissociation energies were obtained and the qualitative form of the curves investigated.

Despite the difficulty of calculating accurately the interaction energies of excited electronic states of weakly bound systems, the information derived about these electronic states by the spectroscopic experiments and the *ab initio* calculations agree reasonably well. For the $X^2\Pi$ state, the vibrationally averaged internuclear separation is calculated to be *ca.* 0.1 Å larger than the value derived from the experimental rotational constant B_0''.

The most interesting result uncovered in this collaborative study is the presence of a barrier in the $B^2\Sigma^+$ electronic state. Such barriers, which have been observed in HgAr[14] and inferred in AlAr[4], have been explained as arising from an attractive dispersion interaction at long range, followed by repulsion between the rare gas and the *ns* Rydberg electron at somewhat shorter distances, and then a strong attractive interaction between the rare gas and the M^+ ion core at even shorter distances, where the rare gas atom has penetrated inside the first node of the diffuse *ns* electron.[4, 14] Unfortunately, our *ab initio* study was unable to support such a simple physical explanation of the appearance of a well

2

COMPLETED PROJECT SUMMARY

TITLE: The Interaction of Group IIIA Atoms with Small Molecules

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D. E. Manolopoulos and M. H. Alexander, "Quantum Flux Redistribution during Molecular Photodissociation," J. Chem. Phys. 97, 2527-2535 (1993).

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M. H. Alexander, C. Rist, and D. E. Manolopoulos, "The Study of Flux Redistribution during Molecular Photodissociation: Adiabatic and Diabatic Analyses and Application to the Dissociation of CH_3I," J. Chem. Phys. 97, 4836-4845 (1992).

C. Rist and M. H. Alexander, "Adiabatic Representations for the Study of Flux Redistribution during Photodissociation Involving Coupled Electronic States: The Effect of Vibrational Excitation on the Photofragmentation of CH_3I," J. Chem. Phys. 98, 6196-6207 (1993).

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M. H. Alexander, S. Gregurick, and P. J. Dagdigian, "Potential Energy Surfaces for the Interaction of $BH(A^1\Pi)$ with Ar and a Theoretical Interpretation of the Electronic Spectrum of the ArBH van der Waals Complex," J. Chem. Phys. 101, 2887-2902 (1994).

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ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The main goal of this project has been the theoretical and experimental investigation of the non-bonding interactions of the boron atom, and small boron-containing radicals, with the hydrogen molecule and other species. The major experimental accomplishments have involved the elucidation of the spectroscopy of weakly bound complexes of these species and the study of bimolecular collisions of electronically excited boron atoms. The concurrent theoretical work consisted of the calculation of potential energy surfaces of interaction and the development of new methods for the study of the dynamics of van der Waals molecules and of molecular photofragmentation.

We have characterized the interaction of boron atoms, in the ground 2p and excited 3s electronic states, with argon through a combination of free jet laser spectroscopy experiments and quantum chemistry calculations. The experiments have involved recording laser fluorescence excitation spectra, to characterize the excited electronic state correlating to B(3s) +Ar, and bound – free emission spectra, to characterize the repulsive portions of the Π and Σ electronic states correlating to B(2p) + Ar. The experimental results were compared with the results of quantum chemistry calculations of these potential energy curves in order to derive interaction energies consistent with the experimental observations.

The non-bonding interaction of B(2p) with H_2 was theoretically investigated through the calculation of the three resulting adiabatic potential energy surfaces. The absolute minimum was predicted to occur in C_{2v} geometry with B_2 electronic symmetry. A

transformation to an approximate diabatic representation was carried out, in which the three states are characterized by the orientation of the B 2p orbital with respect to the B–H_2 axis. These B–H_2 potential energy surfaces were used to investigate the structure and energetics of clusters of atomic boron with H_2 molecules. It is found that the attractive interaction for the approach of H_2 in a plane perpendicular to the orientation of the B 2p orbital governs the features of small $B(p-H_2)_n$ clusters. The interaction of electronically excited B atoms with H_2 was experimentally investigated through observation of BH chemiluminescence from this reaction.

The non-bonding interaction of the BH radical, in its ground and first excited electronic state, with argon was also elucidated through collaborative experimental and theoretical study. The laser fluorescence excitation spectrum of the ArBH complex was recorded, and the observed bands rotationally analyzed. The relevant potential energy surfaces were computed and used to derive theoretical vibrational energies in the two electronic states of ArBH. The pattern of vibrational energies was found to be quite complicated because the interaction in the excited (Π) electronic state depends strongly on whether the electron in the outermost π orbital lies in or is perpendicular to the triatomic plane. These calculations provided a framework to interpret the experimental observations. A similar experimental and theoretical investigation of the interaction of the isovalent AlH radical with Ar was also carried out. These results was also used to interpret the experimentally observed electronic spectrum of the KrAlH complex.

We have also extended our recently developed quantum flux method for the study of mechanisms of molecular photodissociation to the calculation of the current density.

inside the barrier. Since this well appears only when triple and quadruple excitations out of the multi-reference wavefunction are included in the configuration interaction wavefunction, the origin of this well must reflect some subtle interplay between the differential electron correlation and charge polarization effects which occur as the B and Ar atoms approach.

By scaling the long- and short-range portions of the *ab initio* $B^2\Sigma^+$ potential energy curve to the experimental RKR curve, it was possible to model well the spectrum of the broadened, quasi-bound levels.

3. *Observation and Analysis of Bound – Free Emission.* We also inserted a 1/4 m monochromator into the detection train and obtained BAr bound – free emission spectra for the excitation of various $^{11}\text{BAr}(B^2\Sigma^+)$ vibrational levels in order to characterize experimentally the repulsive portions of the $X\ ^2\Pi$ and $A\ ^2\Sigma^+$ potential energy curves.[7] Because of the large differences in equilibrium internuclear separations, this emission occurs mainly to the repulsive walls of the lower states. With our *ab initio* calculations of the potential curves for the relevant electronic states in BAr and associated transition electronic dipole moments,[6, 7] we were able to compare simulated spectra with the experimental observations. The simulations involved a prior determination of the bound $B^2\Sigma^+$ and continuum $X^2\Pi$ and $A^2\Sigma^+$ vibrational wave functions. By shifting the calculated repulsive potentials of the lower $X^2\Pi$ and $A^2\Sigma^+$ states inward by 0.2 Å, we were able to reproduce well the locations of the extrema and the relative intensities in the experimental spectrum. This shift is consistent with our previous observation that the *ab initio* calculations slightly overestimated the vibrationally averaged internuclear separation in the $X^2\Pi$ state.

As an offshoot of this theoretical work, the calculated description of the repulsive walls of the $X^2\Pi$ and $A^2\Sigma^+$ BAr potential curves, and the bound portion of the $B^2\Sigma^+$ curve, are being used by Boatz and Fajardo[15] at the Air Force Phillips Laboratory in Monte-Carlo simulation studies of the electronic spectra of B atoms trapped in solid Ar matrices. It has been found by several workers[16-18] that in matrices the boron atomic transitions are significantly shifted from their gas-phase values.

3

Direct Measurement of the BAr($X^2\Pi$) Spin–Orbit Splitting. In considering the interaction of atoms in states with nonzero spin-orbit splittings with noble gas partners, it is usually assumed[19, 20] that the neither the spin-orbit interaction nor the electronic orbital motion of the p electron(s) are unaffected by this weak interaction. We have followed this "pure-precession" approximation[21, 22] in our initial laser fluorescence excitation study of BAr[6] since the beam internal temperature was so cold that only the ground $X^2\Pi_{1/2}$ spin-orbit manifold was observed. In further experiments, our apparatus was improved sufficiently so that the excited $X^2\Pi_{3/2}$ manifold could be observed, through excitation of the $B^2\Sigma^+ - X^2\Pi_{3/2}$ (7,0) subband.[8]

The spin-orbit splitting constant A for ^{11}BAr($X^2\Pi$, v=0) was determined to equal $10.88 \pm 0.08(1\sigma)$ cm^{-1}. This is close to a simple estimate[22] of this splitting, $(2/3) \Delta E = 10.17$ cm^{-1}, where ΔE is the atomic boron $2p$ $^2P_{3/2} - {}^2P_{1/2}$ spin-orbit splitting. Explicit consideration of the mixing of the ground $X^2\Pi$ and low-lying $A^2\Sigma^+$ electronic states, both of which correlate with the B($2p$ ^{2}P) + Ar atomic asymptote, yields a theoretical estimate of the $X^2\Pi$ spin-orbit splitting of 10.62 cm^{-1}. The close agreement of the experimental value of A with this estimate suggests that neither the spin-orbit interaction nor the electronic orbital motion of the boron $2p$ electron is strongly affected by the weak, nonbonding B–Ar interaction.

B. Investigation of Other B – Rare Gas Interactions

We have also sought to observe the laser fluorescence excitation spectra of several other boron – rare gas van der Waals complexes. We have attempted, thus far unsuccessfully, to detect BNe complexes in supersonic beams seeded in He/Ne mixtures with atomic spin-orbit temperatures as low as 3 K. The BNe ground state binding energy D_0 is estimated by concurrent exploratory *ab initio* calculations to be quite small (≈ 18 cm^{-1}).

We have also observed features which we believe correspond to fluorescence excitation of BKr$_n$ complexes. Since the BKr binding energy is expected to be less than that for Kr$_2$, we have carried out these experiments by first setting up the apparatus to generate BAr complexes in a He/Ar flow. Then a small flow of Kr is added to the gas flow

through a flowmeter. We have observed the loss of the BAr signal as the Kr is added, and the concomitant growth of small signals which correlate with 2 separate molecular carriers. The complexity of the observed bands precludes either of these as the diatomic BKr complex. The most highly structured of these features is presented in Fig. 1. In view of the complexity of this feature and our lack of knowledge of the size of the cluster(s) involved, we have not attempted any analysis of this spectrum.
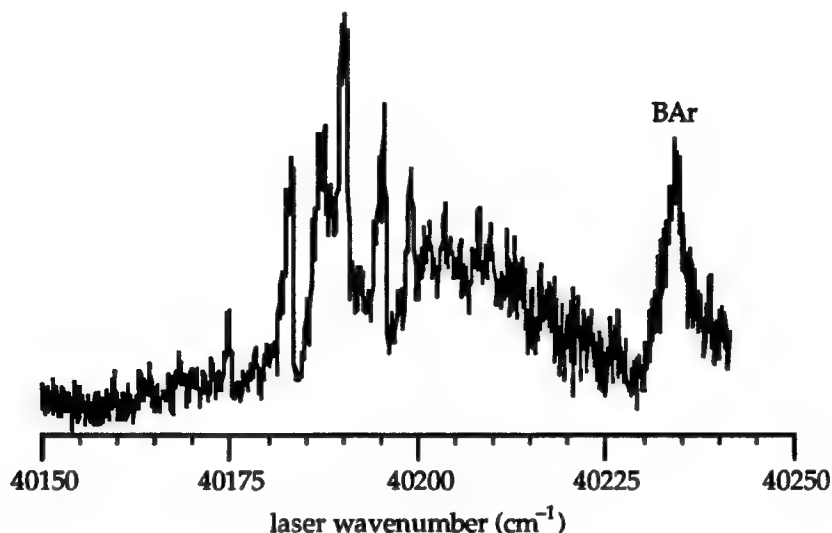

Fig. 1. Laser fluorescence excitation spectrum of a feature assigned to a BKr_n cluster. The feature marked "BAr" is the $B - X$ (8,0) band of BAr and appears in the spectrum because the BAr complex was incompletely titrated away with the addition of Kr to the gas flow.

We suspect that the BKr complex is not kinetically stable in the supersonic flow and is readily converted into higher clusters, presumably BKr_n. This behaviour is similar to that observed by Heaven and co-workes for complexes of CN with Ar.[23] The bimolecular ArCN complex could not be observed in flows of Ar containing the CN radical. However, at high Ar backing pressures, a broad unstructured feature could be observed. From temporally and spectrally resolved observations of the fluorescence emission, these authors concluded that the CN was bound to the outside of a Ar_n cluster.

C. *Ab initio* Investigation of the B–H$_2$ Interaction

Motivated by our experimental work on reactions of electronically excited B atoms with H$_2$,[24] and on the spectroscopy of boron in molecular hydrogen matrices,[18] we have

undertaken the *ab initio* determination of the potential energy surfaces which are accessed by the approach of H_2 to B in its ground ($2s^2 2p$ ^2P) electronic state.[25] The complicating, and challenging, feature of the B$\cdots H_2$ system, as compared to the interaction of an S-state atom [Li($2s$) or Mg($3s^2$ ^1S)] with H_2, is the additional complexity introduced by the threefold degeneracy of the $2p$ orbital. This gives rise to three *adiabatic* potential energy surfaces. Initial CASSCF calculations were carried out to demonstrate the existence of a substantial barrier preventing rearrangement of the B$\cdots H_2$ van der Waals adduct into the known BH_2 molecule. Subsequently, multi-reference configuration-interaction calculations were performed of the three adiabatic potential energy surfaces. The minimum was predicted to occur in C_{2v} geometry with an electronic symmetry of $^2B_2$.

An approach originally introduced by Rebentrost and Lester for the F(^2P) + H_2 system,[26] was used to obtain the transformation to an approximate diabatic representation, in which the three states are characterized by the orientation of the B $2p$ orbital with respect to the B – H_2 axis. The resulting *four* diabatic potential energy functions were then expanded in terms of Legendre and associated Legendre polynomials.

For the interaction of p-H_2 with the B atom, the spherical symmetry of the rotational ground state ($j = 0$) reduces the triatomic system into the interaction of a ^2P atom with a closed-shell, spherical target. Since the spin-orbit constant of the B atom is so small, the lowest state of the B$\cdots p$-H_2 system is governed almost exclusively by the lower (Π-state) B$\cdots p$-H_2 potential. Because of the high zero-point energy of this light system, there exists only one bound vibrational level, with a dissociation energy of ~ 25 cm^{-1}.

Our calculations on the van der Waals region of the BH_2 system complemented concurrent *ab initio* work by Roberta Saxon at SRI International (also supported by the AFOSR HEDM program), which was aimed at the exploration of the topology of the ground and electronically excited potential energy surfaces of the BH_2 *molecule* in the region of its equilibrium geometry.[27]

D. Modeling of B–$(H_2)_n$ Complexes

We used the above information on the B$\cdots H_2$ potential energy surfaces to investigate the structure and energetics of clusters of atomic boron with H_2 molecules.[28] We assumed

that the underlying potential energy surfaces could be built up as pairwise interactions, with a simple geometrical treatment of the electronic aspect of the interaction.[19, 25, 29] The latter implies an anisotropic B–H_2 interaction, resulting from the non-sphericity of the valence unpaired p-electron on the B atom. This approach follows on earlier work of Balling and Wright[29] and represents a novel approach to the study of clusters involving at least one open-shell atom.

We predict the B–H_2 interaction to be more attractive when the H_2 approaches the B atom in a plane perpendicular to the orientation of the B $2p$ orbital. It is this attractive interaction which governs the features of the small B(p-H_2)$_n$ clusters. With this pairwise additive PES we used classical molecular dynamics[30] and quantum diffusion Monte-Carlo (DMC)[31-33] techniques to investigate the structure and stability of small B(p-H_2)$_n$ clusters. The DMC calculations predicted the largest gain in stability to occur for the $n = 5$ cluster. Because of the large zero-point energy and the relatively shallow minima, it is unlikely that additional bound vibrational states will be supported.

The classical studies of the minima in the potential surfaces for B clustered with 2–8 (p-H_2) molecules show gains in stability of $70 - 110$ cm^{-1} when compared to the energy of the cluster with one fewer hydrogen molecule. The strong B–H_2 interaction governs the structure of the relatively small complexes considered ($n < 9$). The hydrogens distribute themselves so that the distribution of B–H_2 distances resembles closely that in the B(p-H_2) complex. Because of the strong B–H_2 bonding, compared to the much weaker H_2–H_2[34] or Li–H_2[35, 36] interaction, in the B(p-H_2)$_n$ clusters the B atom tends to be fully solvated. By contrast, in the modeling work of Klein and co-workers[36] on Li(p-H_2)$_n$ clusters, the Li atom was invariably found at the periphery of the cluser.

Collaborative work with the group of Benny Gerber at Irvine (also supported by the AFOSR HEDM program), showed that for clusters involving p-H_2 the effects of the anisotropy of the interaction on the wavefunction and energy are virtually negligible and result in a lowering of the zero point energy by only a few percent.[28] This justifies the use of an isotropic model in the investigation of the main structural and energetic properties of the larger B(p-H_2)$_n$ clusters.

These heterogeneous $B(p\text{-}H_2)_n$ clusters represent a bridge between highly quantum clusters, such as those of $p\text{-}H_2$ or He, in which the large zero-point energy and lack of structured minima dominate result in broad, unstructured probability distributions of the geometrical parameters, and those of heavier atoms, with deeper minima, in which relatively few structures play an important role. In $B(p\text{-}H_2)_n$ the probability distributions of the geometric parameters reflects an interplay between the light mass of the hydrogen ligands, which renders the vibrational wavefunctions diffuse, and the relative strength of the $B\text{-}H_2$ interaction, which imposes significant energetic constraints on the structure of the cluster.

E. Bimolecular Collisions of Electronically Excited B Atoms

We have also studied bimolecular reactive and inelastic collisions of electronically excited boron atoms with H_2 and other species.[24, 37] While the reaction of ground state boron atoms with H_2 is substantially endothermic, reaction of $B(3s\ ^2S)$ is sufficiently exothermic to allow formation of $BH(X^2\Sigma^+, A^2\Pi)$, as well as to yield $B(2p\ ^2P) + H + H$. In order to study such bimolecular collisions, ground state boron atoms were prepared photolytically in a cell by the 266 nm multiphoton photolysis of BBr_3. Atoms in the excited $3s\ ^2S$ state were then prepared by laser excitation on the $3s\ ^2S \leftarrow 2p\ ^2P$ transition at 249.8 nm. Because of the short radiative lifetime (~ 3 ns) of this level, we could not determine its quenching rate constants by time-resolved techniques.

We have explored the reactivity of a higher state of boron, namely the $4p\ ^2P$ state, which can be prepared by laser excitation of the 3s ^2S level. We find that the quenching rate constants for the $4p\ ^2P$ level by H_2, D_2, and other molecules are quite large ($\sim 10^{-9}$ molecule^{-1} cm^3 s^{-1}),[37] as expected from the diffuse nature of the Rydberg $4p$ orbital. We have also observed BH and BD chemiluminescence from the $B(4p\ ^2P) + H_2$ and D_2 reactions.[24] We find formation of several product electronic states $[A^1\Pi, b^3\Sigma^-, C'^1\Delta]$ and a large isotope effect on the chemiluminescence cross sections, both of which are indicative of nonadiabatic effects in the reaction dynamics.

8

F. Experimental and Theoretical Study of the Ar–BH Interaction

Our source of boron atoms in the supersonic beam experiments is the 193 nm photolysis of diborane. We have been exploring another important fragment from this photolysis process, namely the BH diatomic molecule, which is conveniently detected by laser fluorescence excitation in its $A^1\Pi - X^1\Sigma^+$ band system near 433 nm. We have observed BH molecules in our supersonic beam and, in addition, have detected for the first time the ArBH van der Waals complex and recorded its electronic spectrum, which occurs in the region of the BH $A - X$ (0,0) band.[38] We have observed 12 Ar BH bands with resolved rotational structure and 9 diffuse bands. We believe that the upper levels of the latter bands are predissociative since they lie above the lowest excited asymptote [BH($A^1\Pi$, $v'=0$, $j'=1$) +Ar]. From the observed convergence limits of these bands and the shifts from the BH diatom transition, we estimate the ground and excited state binding energies as D_0'' ≈ 92 cm^{-1} and $D_0' \geq 176$ cm^{-1}. We have rotationally analyzed the sharp observed ArBH bands and, with the help of theoretical calculations described below, assigned van der Waals stretch and bend vibrational quantum numbers to the observed levels.

In conjunction with these experiments, we have carried out multi-reference, configuration interaction calculations of the potential energy surfaces (PES's) for the interaction of Ar with the BH diatom in its two lowest electronic states ($X^1\Sigma^+$, $A^1\Pi$).[39] While complications due to the electron spin are avoided since BH has singlet spin multiplicity, one difficulty in understanding the pattern of observed vibrational levels is the large difference in the ArBH($A^1\Pi$) interaction energies when the unpaired π electron lies in or perpendicular to the triatomic plane.

The *ab initio* calculations were carried out on both workstations in our own group and the CRAY YMP-8 and CRAY C90-16 supercomputers at the U. S. Army Waterways Experiment Station, through a grant of time under the patronage of the Air Force Phillips Laboratory. These potential energy surfaces were used in a novel adiabatic analysis of the rovibronic levels of the ArBH complex in its ground and first excited electronic states. This work benefitted from our prior expertise in the quantum formulation of collisions involving diatomic molecules in Π electronic states.[39] In particular, in a joint paper[39] we have underlined the usefulness of our *adiabatic bender* analysis in which one first

9

diagonalizes the full Hamiltonian as a function of the atom-molecule distance, and then subsequently obtains the vibrational eigenvalues of the resulting one dimensional adiabatic bender potentials. These theoretical investigations of ArBH have been immensely helpful in providing a framework with which to interpret the contemporaneous experimental results. In particular, the most strongly bound states of the ArBH($A^1\Pi$) correspond to internal (helicopter like) rotor motion of the BH moiety bound on the more attractive (A'') of the two ArBH(A) PES's.

More recently, in projects supported by other agencies, we have used this adiabatic bender model in the analysis of fluorescence excitation spectra of weakly bound complexes of other diatomic hydrides (ArCH and ArNH).[40, 41]

G. Experimental and Theoretical Study of the AlH – Rare Gas Interactions

We have also extended our study of non-bonding interactions of BH to the study of these interactions involving the isovalent AlH radical. This species was prepared in a supersonic beam expansion by 193 nm photolysis of trimethylaluminum. We have detected AlH and van der Waals complexes with Ar and Kr by laser fluorescence excitation in the spectral region around the AlH $A - X$ (0,0) band.[42, 43] For both complexes, we observed a number of bands, both sharp and diffuse. The binding energies were found to be greater than for ArBH; in particular, we obtained $D_0'' = 124$ and 198 cm^{-1} for the ground electronic states of ArAlH and KrAlH, respectively. Rotational analyses of the sharp bands yielded vibrationally averaged separations and angular momentum projection quantum numbers.

In order to interpret the observed complex pattern of vibrational energies and to assign bend-stretch quantum numbers, multireference, configuration-interaction calculations of the PES's for the interaction of Ar with AlH($X^1\Sigma^+$, $A^1\Pi$) were carried out.[44] As in our collaborative study of ArBH, slightly modified versions of these PES's were employed to calculate the bend-stretch energies of ArAlH(X, A). With these calculations, it was possible to assign the sharp bands observed in the ArAlH spectrum.[42] With the excellent signal-to-noise ratio in the experiment, it was possible to observe several

hot bands, thus providing direct information on vibrational spacings in the ground electronic state of the complex.

It was also possible to assign the bands observed in the spectrum of KrAlH.[43] Despite the expected larger van der Waals radius for Kr *vs*. Ar, we found that the vibrationally averaged AlH–Rg separation is slightly *smaller* in KrAlH than in ArAlH. We believe that this smaller atom–diatom separation reflects an inward shift of the onset of the repulsive interaction because of an increased attractive interaction, as reflected by a larger binding energy for KrAlH *vs*. ArAlH.

H. Observation of the Br$_2$ D' – A' Band System

In our initial attempts to observe the BAr spectrum, several different approaches for the generation of B atoms were tried. Prior to using diborane as a photolytic source of B atoms, we initially employed BBr$_3$ as a precursor. While a strong B atom signal was observed, no van der Waals bands were found. By contrast, an extensive series of molecular bands was observed. These have been identified as the Br$_2$ D' – A' band system. The lower state of this system is the poorly characterized $\Omega=2_g$ state expected from the interaction of two ground state Br atoms.[45] We are presently collaborating with Joel Tellinghuisen (Vanderbilt University) and Michael Heaven (Emory University) to analyze these bands in order to extend our knowledge of these Br$_2$ electronic states.

I. A Quantum Flux Method to Analyze Photodissociation Dynamics

In collaboration with David Manolopoulos of the University of Nottingham (UK), we have extended our novel quantum flux method[46, 47] to the study of mechanisms of molecular photodissociation.[48-50] The current density associated with the photofragment wavefunction provides a means to investigate the dependence of the photodissociation process on the interfragment separation: flux rises in the various channels of the unbound excited state as the initially bound fragments move through the region where the photon is absorbed, and then is redistributed because of interactions in the excited state. For dissociation involving multiple electronic states, each with internal (vibrational or ro-vibrational) degrees of freedom, it is more physically meaningful to analyze the flux in a

11

basis which is *adiabatic* in the nuclear degrees of freedom but *diabatic* in the electronic degrees of freedom.[48, 50] We have shown how this can be implemented with application to a two-dimensional model for the photodissociation of CH_3I.[48-50] This flux analysis revealed that the degree of adiabaticity in photodissociation displays a subtle dependence on the energy which would be lost in a conventional wavepacket analysis, in which mechanistic information is averaged over all the energies accessed in the photoexcitation.

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14

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